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RELATED PCT APPLICATION NUMBER: *PCT/US03/27439*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

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Docket No. 01-2-118

"Express Mail" mailing label number EL 774686466 US
Date of Deposit September 4, 2002

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53 (c).

FULL NAME OF INVENTOR Maria B. Winnicka
Residence 47 Pleasant St., Sayre, PA 18840

TITLE OF INVENTION

Non-sag Molybdenum-Lanthana Sheets

CORRESPONDENCE ADDRESS

Robert F. Clark
OSRAM SYLVANIA INC.
100 Endicott Street
Danvers, MA 01923

ENCLOSED APPLICATION PARTS

X Specification Number of Pages 20 including Drawings.

METHOD OF PAYMENT

The Commissioner is hereby authorized to charge the Provisional filing fee of $160.00 to Deposit Account Number 15-0689.

Was the invention made by an agency of the United States Government or under a contract with an agency of the United States Government?

X No ___ Yes, the name of the U.S. Government agency and the Government contract number are:_____

Respectively submitted,

Robert F. Clark
Reg. No. 33,853

9/4/02
Date

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01-2-118

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Maria B. Winnicka ~~et al~~

Serial No. Herewith

Art Unit: Not Assigned

Filed: Herewith

Examiner: Not Assigned

For: Non-sag Molybdenum-Lanthana Sheets

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

EXPRESS MAIL CERTIFICATE

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Express Mail Certificate (1 page)
Provisional Application Cover Sheet (1 page, in triplicate)
Provisional Application Specification (20 pages)
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Robert B. Clark Reg. No. 33,853

Robert B. Clark

(Signature of person mailing paper or fee)

NON-SAG ML SHEETS

Dr. M. B. Winnicka

PROBLEM SOLVED BY INVENTION

The main problem solved by this invention is to enable OSRAM SYLVANIA to produce molybdenum – lanthana sheets in an improved manner as compared with the existing patent by Eck et al. titled "Creep-resistant alloy of high-melting metal and process for producing the same," patent number 4,950,327 dated August 21, 1990. The assignee of the patent is Schwarzkopf Development Corporation, New York, NY.

Another problem solved is the accelerated sagging of molybdenum-lanthana sheets when used at temperatures above 1800°C for at least 1 hour.

TECHNIQUES USED TO SOLVE THE PROBLEM PRIOR TO INVENTION

The above mentioned patent by Eck et al. describes the way of rolling (reforming) of molybdenum –lanthana sheets. It states in Example 4:

"Another alloy according to the invention was produced as follows:

Molybdenum metal powder with grain size of 5 μm was mixed with 2 weight-% $La(OH)_3$-powder with a grain size of 0.4 μm and the mixture was compressed on matrix presses at 3 MN to form sheets with the dimensions 17 cm x 40 cm x 5 cm. Subsequently, the sheets were rolled at reforming temperatures of about 1400°C starting with graduations of about 10% degree of reformation, to obtain a sheet with a final sheet thickness of 1 mm. Following the final recrystallization annealing at about 1900°C, the sheet material had a tiered structural arrangement."

Also, claim 7 of the said patent indicates: "and the resulting powder mixture is compressed and sintered and the resulting sintered body is mechanically reformed with a degree of reformation of at least 85% and is subjected to heat treatments, said sintered body being finally subjected to recrystallization annealing."

HOW WAS PROBLEM SOLVED

The problem of obtaining non-sag microstructure in the sheet was solved by isostatic pressing of a mixture of powders of molybdenum and lanthanum hydroxide, sintering and rolling of the sintered slab in such a way as to exert maximum of 15% of deformation to the slab prior to desired thickness.

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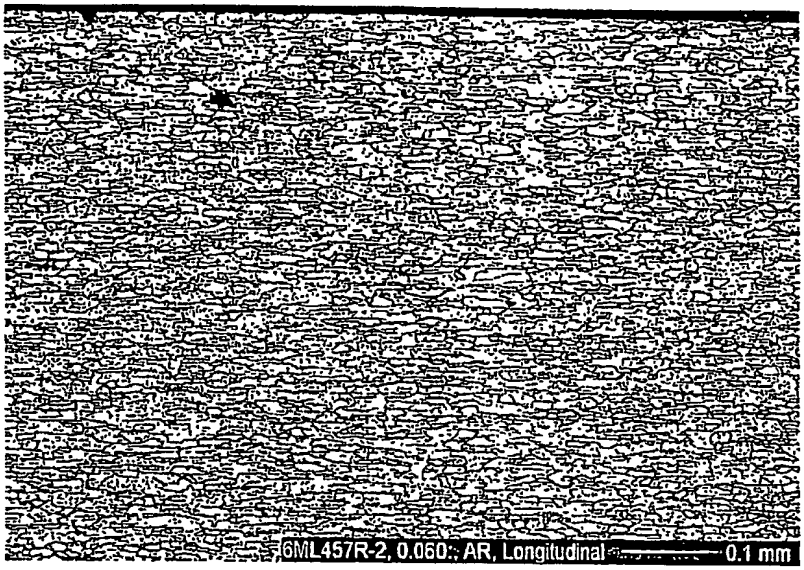
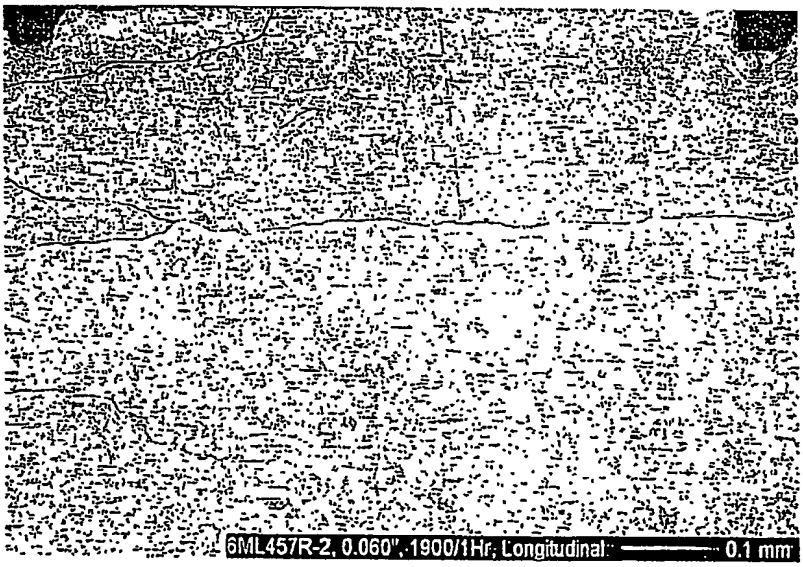
Example 1 provides details of one of such slab.

Pure molybdenum metal powder with grain size of 3.5 μm was mixed with 0.7 weight % of $La(OH)_3$-powder with a grain size of 0.65 μm. The mixture was isostatically pressed at 240 MPa to form a pressed slab with the dimensions 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C, followed by 785°C and finished off at ambient temperature and at thickness of 0.17 cm. The sheet was then recrystallized at 1400°C. Subsequently it was rolled at ambient temperature to the thickness of 0.15 cm. Upon final recrystallization anneal at 1900°C, the sheet material exhibited non-sag microstructure (tiered structural arrangement).





Figures showing as rolled microstructure and after the 1900 C anneal.

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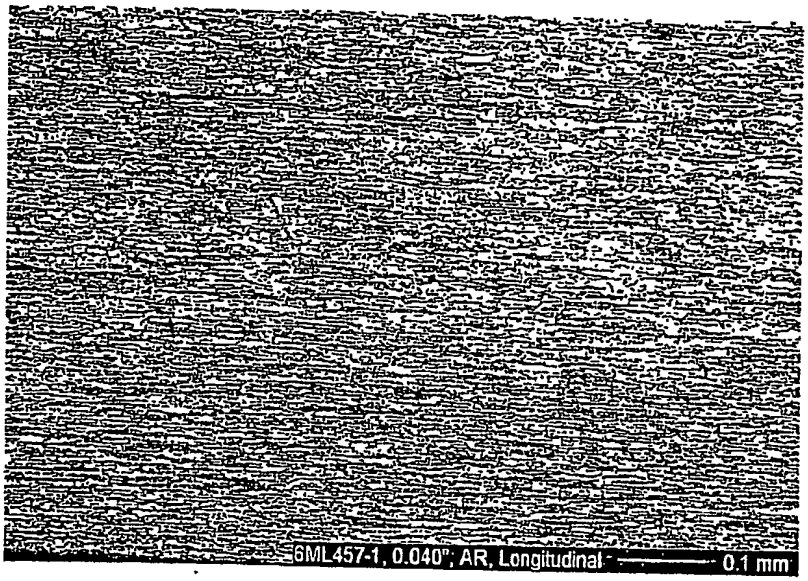
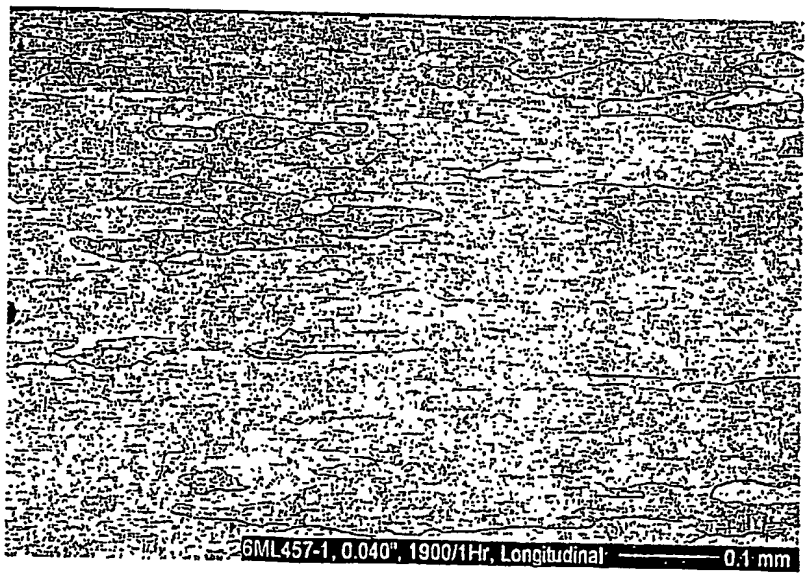
MB 6/20

Example 2 provides details of another such slab

Pure molybdenum metal powder with grain size of 3.5 μm was mixed with 0.7 weight % of $La(OH)_3$-powder with a grain size of 0.65 μm. The mixture was isostatically pressed at 240 MPa to form a pressed slab with the dimensions 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C, followed by 785°C and finished off at ambient temperature and at thickness of 0.12 cm. The sheet was then recrystallized at 1150°C. Subsequently it was rolled at ambient temperature to the thickness of 0.10 cm. Upon final recrystallization anneal at 1900°C, the sheet material exhibited non-sag microstructure (tiered structural arrangement).





Figures showing as rolled microstructure and after the 1900 C anneal.

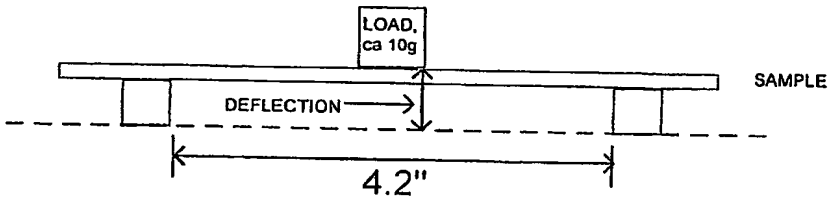
TJP 6/20/01 RPS 6/20/01 MBW 6/20/

Comparison and advantages of my invention vs, Eck et al. patent

The sag test performed at the same time and the same conditions that comprised of two samples of Plansee AG material produced as per Eck et al. patent procedure and two samples of OSRAM Sylvania material produced as per my invention show exactly the same values of deflection for 0.15 cm thick material and negligibly better values of deflection for 0.10 cm thick OSRAM Sylvania material versus Plansee AG material.

Page 11 from Notebook G 34761 is attached

The sag test set-up is shown below



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6/20/

ML material sag tests at 1900 C for 1 hour each run in Centorr furnace
Inside distance between supports was 4.2" All samples were annealed at 1900 C for 1 hour prior to testing

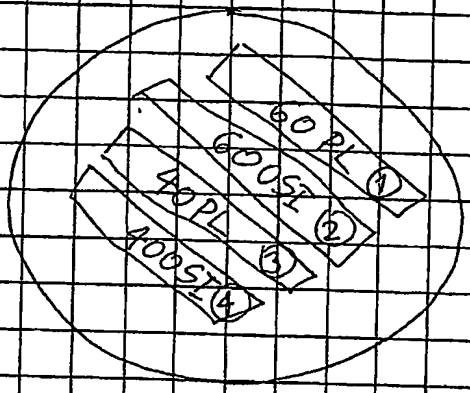
Material	Width	Length	Center Load (g)	Distance from Plate at Start	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Total Sag
60-mil											
Plansee	0.5	5.6	9 9849	0 5	0 4375	0.4375	0.4375	0 4375	0 4375	0 4375	0.0625
OSI	0.5	5 6	9 9894	0 5	0.4375	0.4375	0.4375	0 4375	0.4375	0 4375	0.0625
40-mil											
Plansee	0 5	5 6	9 9706	0.4375	0.421875	0.40625	0 390625	0 390625	0 390625	0.390625	0 046875
OSI	0 5	5 6	9 9825	0.4375	0 421875	0 421875	0 40625	0 40625	0 40625	0.40625	0 03125

6/20/01 PBS 6/20/01 - MBW 6/20/01

The main advantage of this invention as compared with Eck et al. invention is its flexibility with regards to the source of feed material's thickness and hence flexibility in creating the non-sag structure at almost any useful thickness of sheets. The perceived limitation in Eck et al. invention is its need to use very thick starting slabs to create the non-sag structure only after at least 85% reduction in thickness. In the current invention the starting material's thickness needs only to be 18% higher than final desired thickness. Another perceived limitation of Eck et al. invention is the lack of control of desired grain size of non-sag microstructure because the physical phenomenon associated with it is spontaneous. In the case of current invention the grain size of non-sag microstructure can be controlled; from huge grains, as in Example 1 to smaller grains, as in Example 2. The ability to control the grain size is explained in a greater detail in the attached TM 2000-D/ROD0090-TW report.

TM 6/20/01 RPS 6/20/01 MBW 6/20/

4/26/01 1900/1hr runs as Seq tests of 60, 40-mil Plonsee ML and 60, 40-mil over ML wafe
4/27/01
4/30/01
5/01/01



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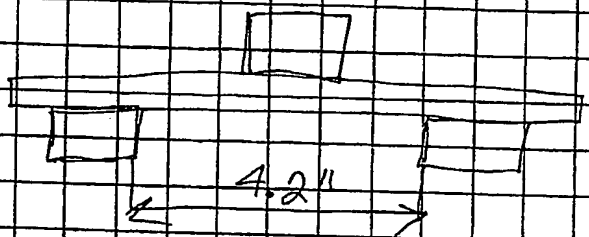

Sample	load
1	9.9849
2	9.9894
3	9.9706
4	9.9825

Sample	Distance at start from plate	4/26 run 1 9:30-2:30pm	run 2 8:45-1:45	run 3	4/27 run 4 8:45am-1:45	4/30 run 5 2pm-
1	8/16"	-1/16	-0	-0	-0	-0
2	8/16"	-1/16	-0	-0	-0	-0
3	7/16"	-25% 1/16	-25% 1/16"	-25% 1/16"	-0	-0
4	7/16"	-25% 1/16	-0	-25% 1/16'	-0	-0

Seq.	Ramp	Soak	time	event
1		20	0:15	2
2		20	0:15	4
3	1900		1:35	4
4		1900	1:00	4
5	20		0:30	4
6		20	1:00	3

6/20/01 RJS 6/20/01

MBA 6/20/

OSRAM SYLVANIA R&D

Technical Memorandum: TM2000-D/ROD0090-TW

Title: Control of the Grain Size in Molybdenum-0.6 wt % Lanthana Sheets

Author(s)/Editor: M. B. Winnicka

Date: 20-December-2000 **Telephone:** 570-268-5416

Location: **FAX:** 570-268-5350

Author(s) Signature: Maria B. Winnicka

Approval:

Project Number: **Pages:** 14

Abstract/Summary:

***Note** - Full text available in Lotus Notes: DA_NOTES2/[RD]/Eng Rpts (1996-Present)*

This report is a follow-up of a recent report TM00-D/ROD0087-TW. It contains the theoretical background on control of the grain size in polycrystalline metals that exhibit recrystallization behavior. Strain-induced Grain Boundary Migration and Exaggerated Grain Growth phenomena are explained. Experimental results are shown. Several grain sizes were achieved in the ML sheets by proper utilization of the deformation vs. heat treatment relationship.

Keywords: molybdenum-lanthana sheet, grain size control, strain-induced grain boundary migration, exaggerated grain growth

COMPANY PRIVATE

6/20/01 RPS 6/20/01

MBW 6/20/0

INTRODUCTION

The recrystallization behavior of metals is inherently connected with prior plastic deformation incurred by the metal. The more plastic deformation the metal received the higher the stored energy level in the metal. Recrystallization behavior is an energy driven phenomenon and the greater the stored energy the more "eager" it will be to recrystallize. The fundamental law of nature is to lower its own energy, to be in as near equilibrium as possible. Therefore, materials that have a lot of stored energy will recrystallize at a lower temperature than materials that are energetically stable. Therefore, the so-called recrystallization temperature is not a physical constant of the material in the same sense as melting temperature or Young's modulus, but it is a conventional temperature derived for technological purpose. It varies depending on particular set of conditions the material underwent prior to recrystallization.

When the undeformed or fully recrystallized material is being cold worked, the density of dislocations increases. In polycrystals the density of dislocations increases first at the grain boundaries and progresses further into the bulk of the grains as the amount of cold work increases. It is then imaginable that by controlling the amount of cold work in the material, the subsequent movement and location of those moving dislocations can be controlled. In the literature there are certain phenomena associated with the different stages of cold work and subsequent heat treatment of the material.

- Strain-induced grain boundary migration phenomenon occurs when the material received small amount of cold work prior to heat treating. In this scenario, the final grain size of the material will be larger because the predominant phenomenon occuring during heat treatment is the anihilation of dislocations at the neighboring grain boundaries causing some of the grain boundaries to disappear. This phenomenon will only occur after a certain amount of cold work (called ξ_{crit}) is received by the material. The values of ξ_{crit} are usually 3 to 10% depending on the material type.
- Recrystallization phenomenon occurs after the material received at least a certain amount of cold work (called ξ_{recr}). The values of ξ_{recr} are always higher than ξ_{crit} and are usually between 20% to 85%. The density of dislocations then is high, the network of dislocations progressed throughout the whole grains. Upon heat treating the dislocation nodules are the nucleation sites for new grains that are dislocation-free. The final grain size is the size of the material prior to cold working.
- Exaggerated grain growth or Secondary recrystallization occurs when the material is cold worked to a great extent, usually 90% or more, called ξ_{exag}. This phenomenon results in big grain size after heat treatment at sufficiently high temperature because after the completion of recrystallization the material still possesses energy and some high angle grain boundaries move at the expense of low angle boundaries.

Based on the above, it is important to note that after the heat treatment causing big grains to form, it is virtually impossible to resolve if the material received high or low amount of cold work.

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A complete, 3-D recrystallization diagram was found in the literature for pure Al. It is presented in Figure 1.

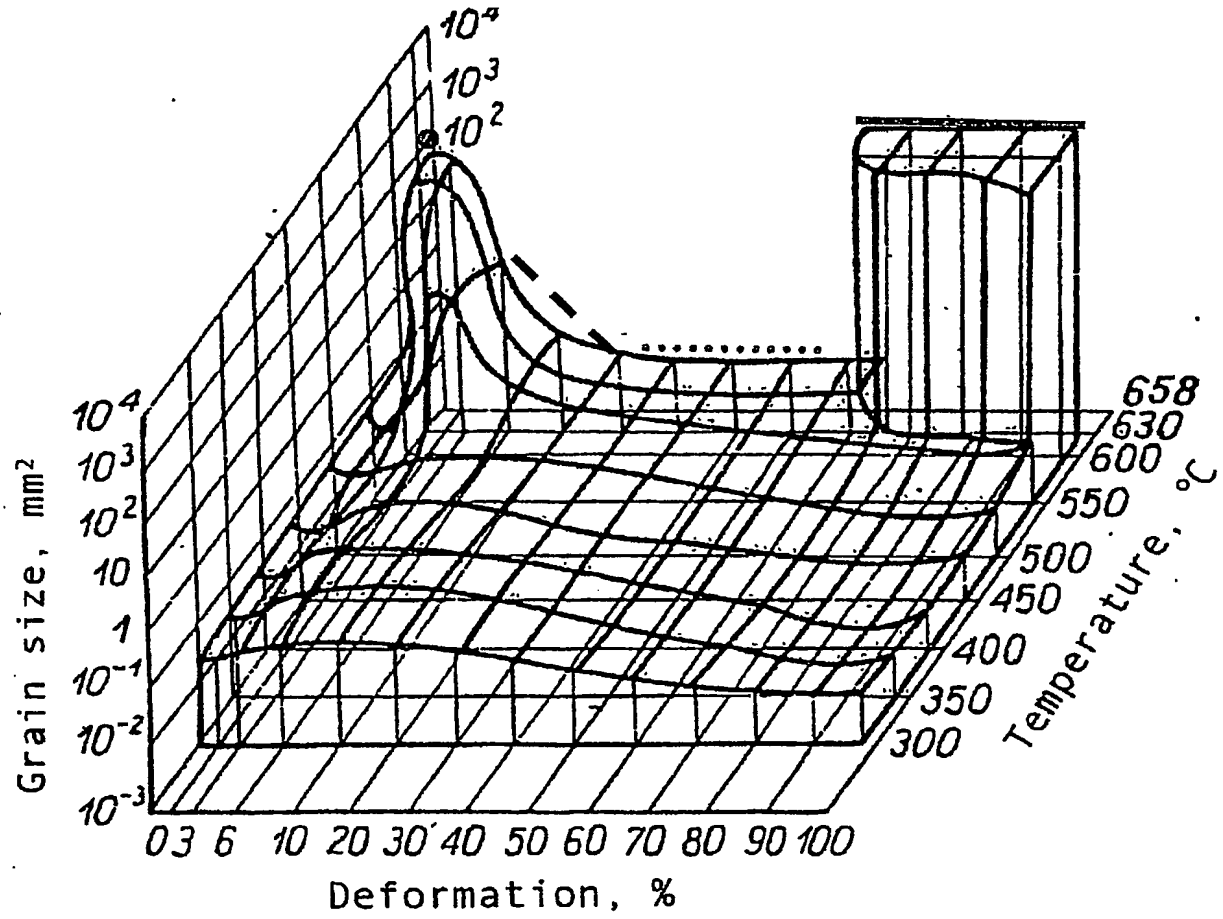

Figure 1: A complete, 3-D recrystallization diagram for pure Al (98.5%) after A.P. Gulayev "Metaloznawstwo", 3rd edition, 1967, p.70.

The following observations can be made from Figure 1:

- for the Strain-Induced Grain Boundary Migration phenomenon to occur in pure Al the value of ξ_{crit} has to be between 2 and 6% and heat treating temperature at least 600°C
- for the Recrystallization phenomenon to occur in Al the value of ξ_{recr} has to be between 20 and 65% and heat treating temperature at least 300°C
- for the Exaggerated Grain Growth phenomenon to occur in Al the value of ξ_{exag} has to be at least 70% and heat treating temperature at least 600°C.

T/C/20/01 RDS 6/20/01

MBW 6/20/0

A diagram for pure Mo, similar to the one presented in Figure 1 was not found in the literature.

It was decided to find out if Mo-Lanthana material will exhibit the above discussed phenomena within the technologically available to us conditions (available furnace temperature capability, controlled % deformation testing). This study was undertaken within the context of achieving a large grain structure in Mo-lanthana material, similar to Plansee AG ML material that is used for Exeter PCA trays.

PROCEDURE

A piece of Mo-lanthana sheet, called 9ML001 A6*), that was stress and strain free at 0.115" thickness was subjected to incremental cold working via rolling. The % cold work put into the material was controlled via vernier setting on the rolling mill. Samples were taken from the sheet after each increment of cold work. All the ML samples were subsequently heat treated at 1800°C for 30 minutes in hydrogen atmosphere.
One sample of pure Mo sheet**) that was stress and strain free at 0.150" thickness and cold worked 96% was also given a high temperature treatment.
*) see Table I in Appendix for the metalworking history of this sample prior to incremental cold working
**) see Table II in Appendix for the metalworking history of this sample prior to 96% cold working

It is important to comment that no cross-rolling was involved in the performed testing, but simple straight rolling.

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RESULTS

Figures 1 and 2 present the microstructures of Plansee material that Exeter currently uses for their PCA trays.

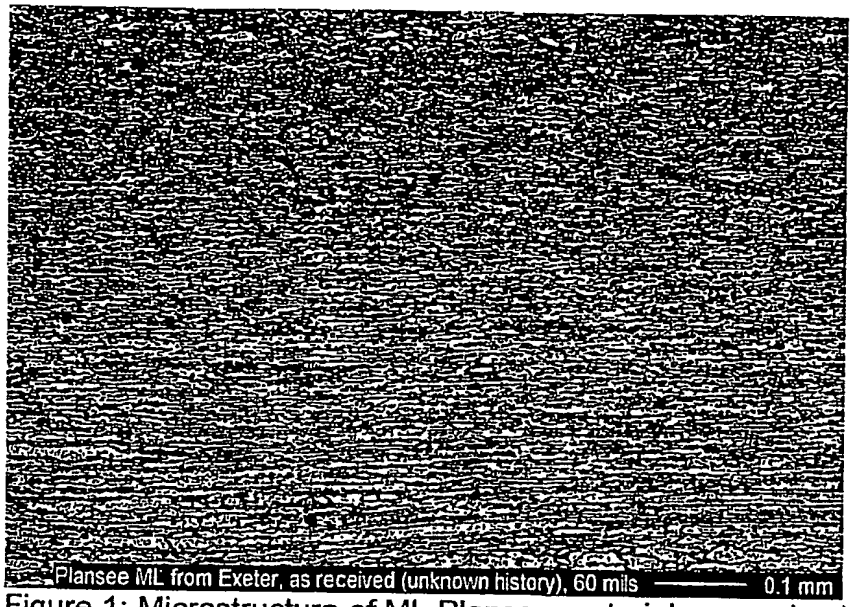

Figure 1: Microstructure of ML Plansee material as-received (unknown history).

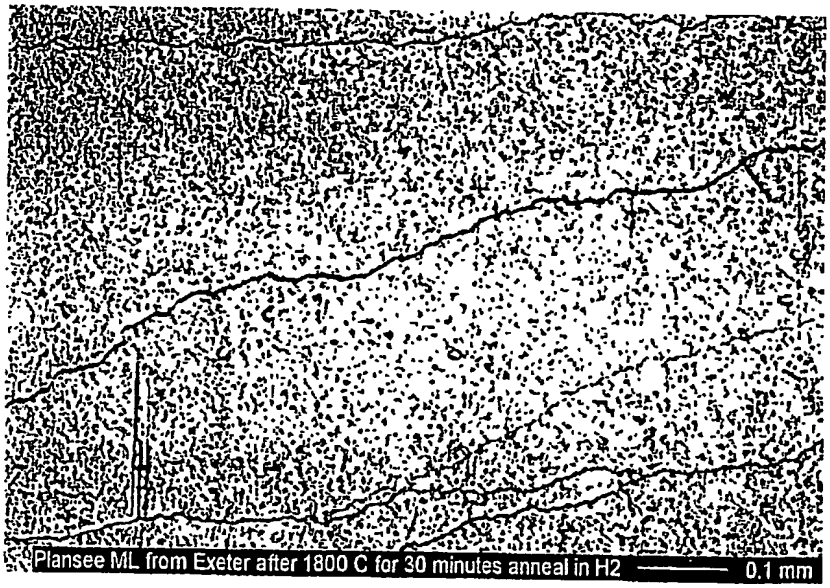

Figure 2: Microstructure of the ML Plansee material after 1800 C/30 min. anneal.

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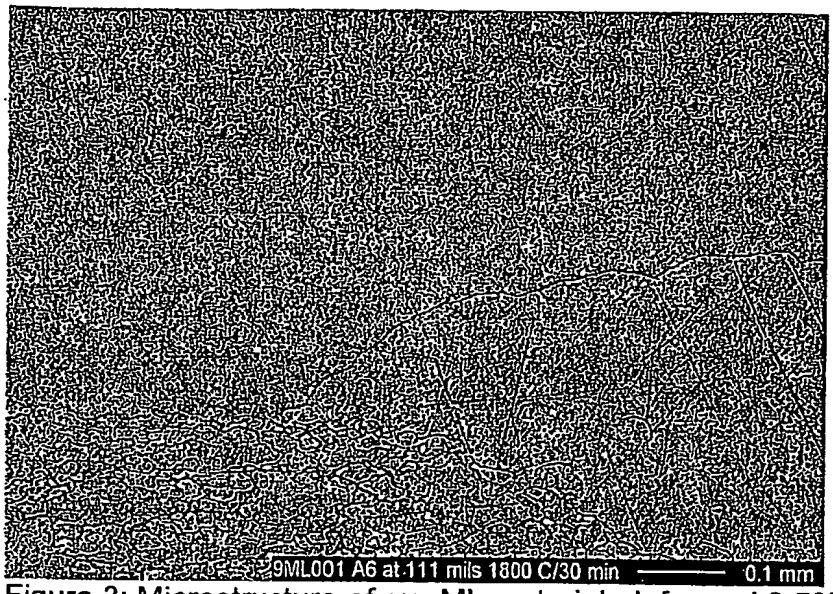

Figure 3: Microstructure of our ML material, deformed 3.5% and heat treated at 1800 C for 30 minutes.

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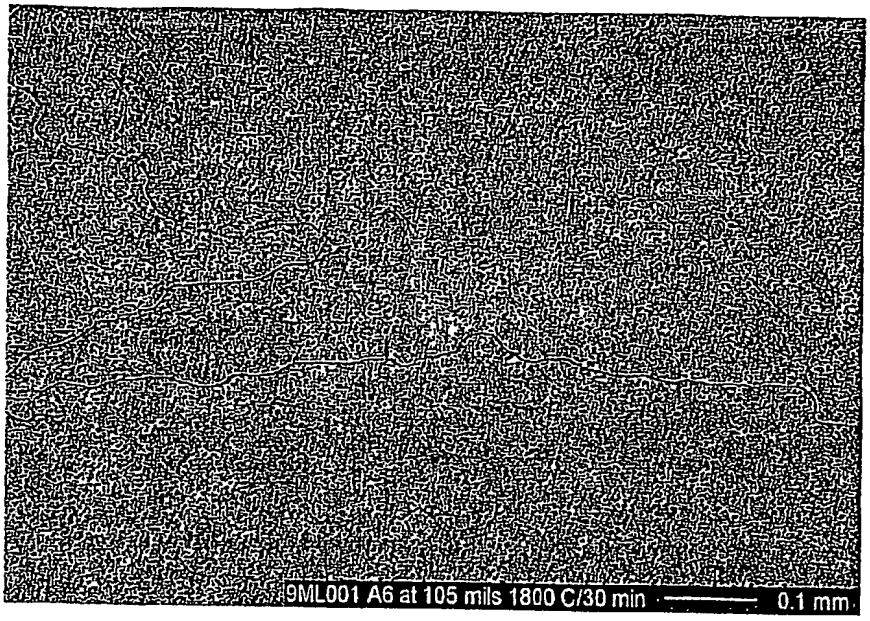

Figure 4: Microstructure of our ML material, deformed 8.7% and heat treated at 1800 C for 30 minutes.

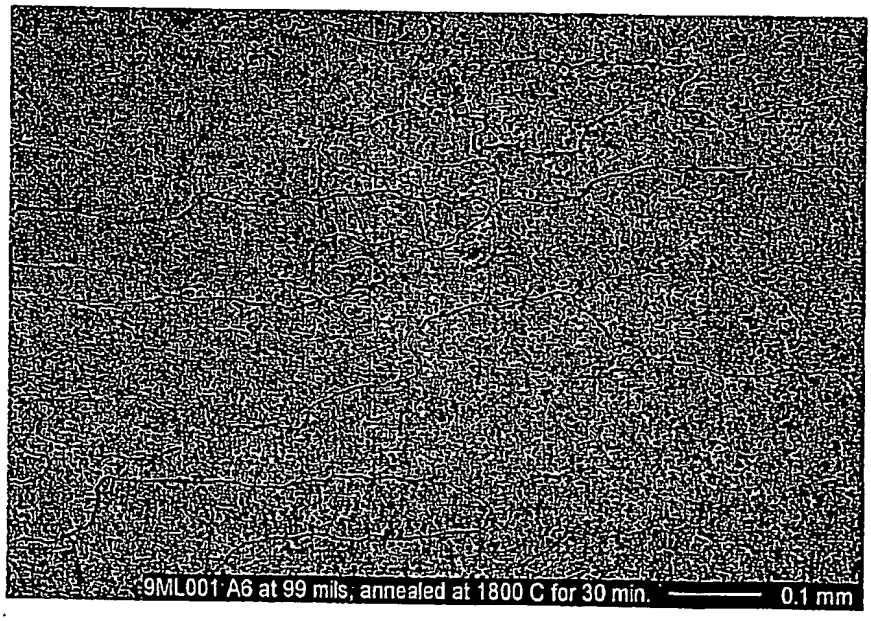

Figure 5: Microstructure of our ML material, deformed 13.8% and heat treated at 1800 C for 30 minutes.

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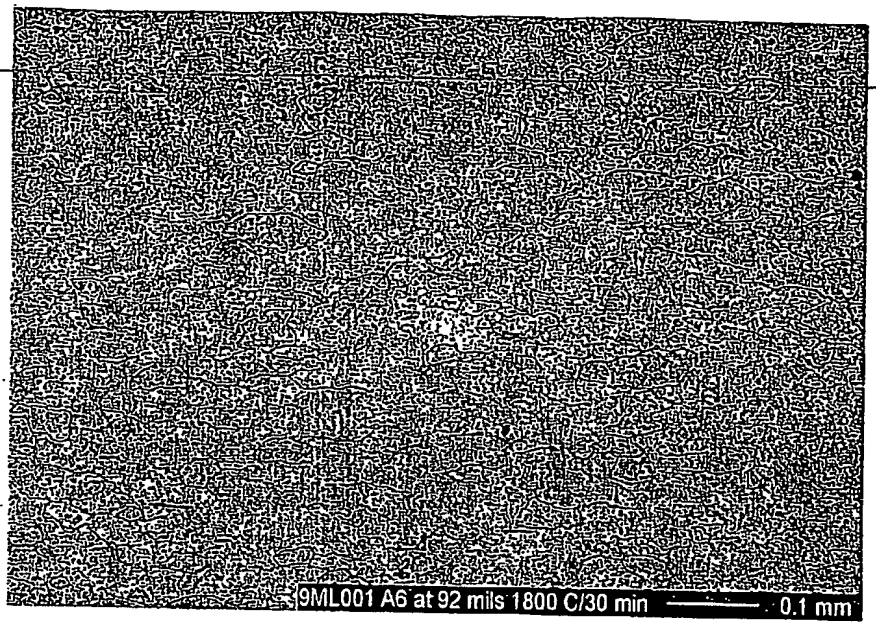

Figure 6: Microstructure of our ML material, deformed 20% and heat treated at 1800 C for 30 minutes.

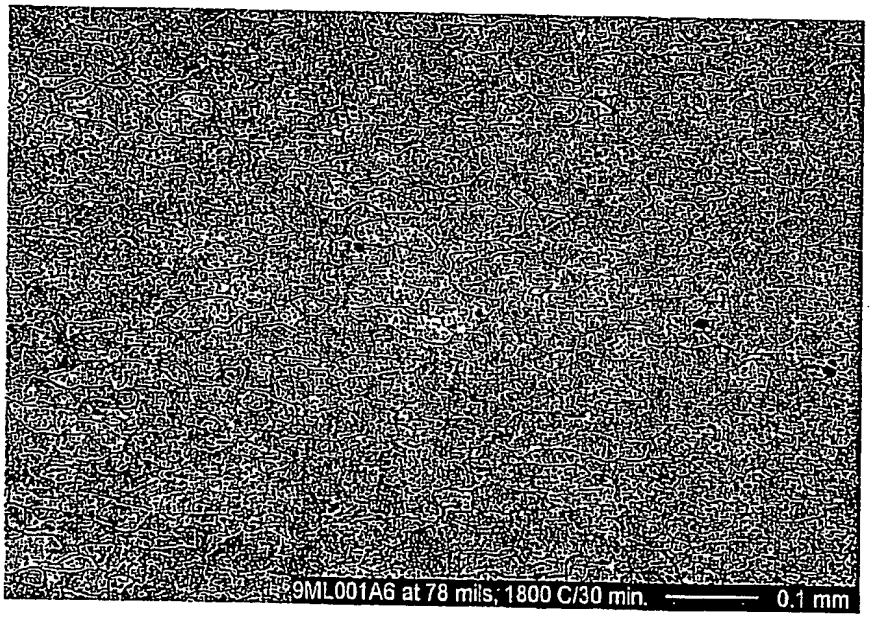

Figure 7: Microstructure of our ML material, deformed 27.5% and heat treated at 1800 C for 30 minutes.

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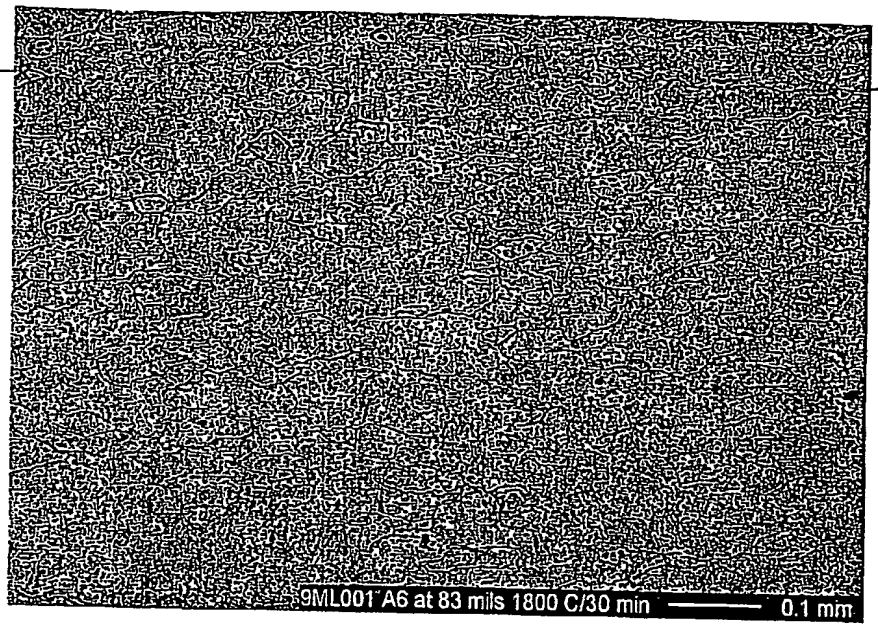

Figure 8: Microstructure of our ML material, deformed 32.3% and heat treated at 1800 C for 30 minutes.

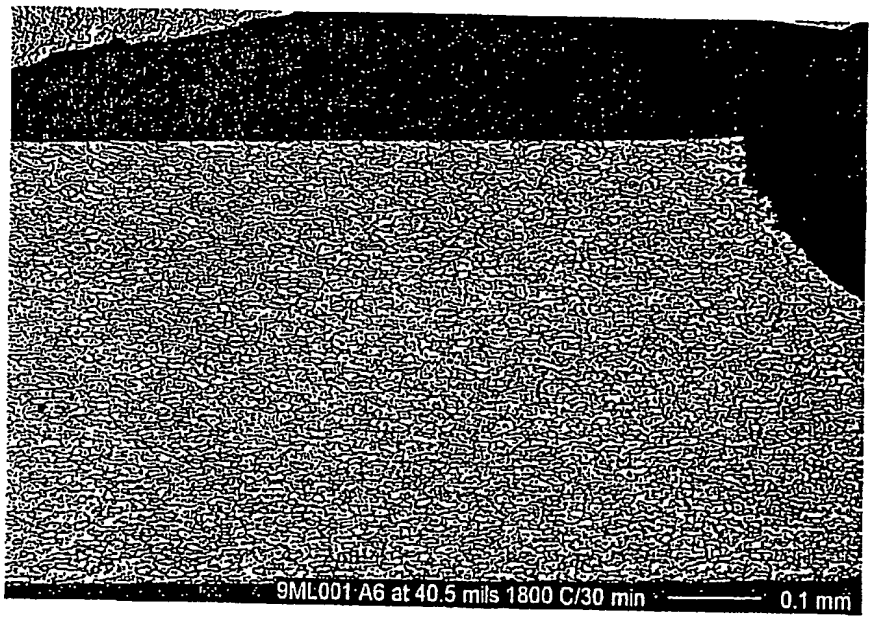

Figure 9: Microstructure of our ML material, deformed 64.8% and heat treated at 1800 C for 30 minutes

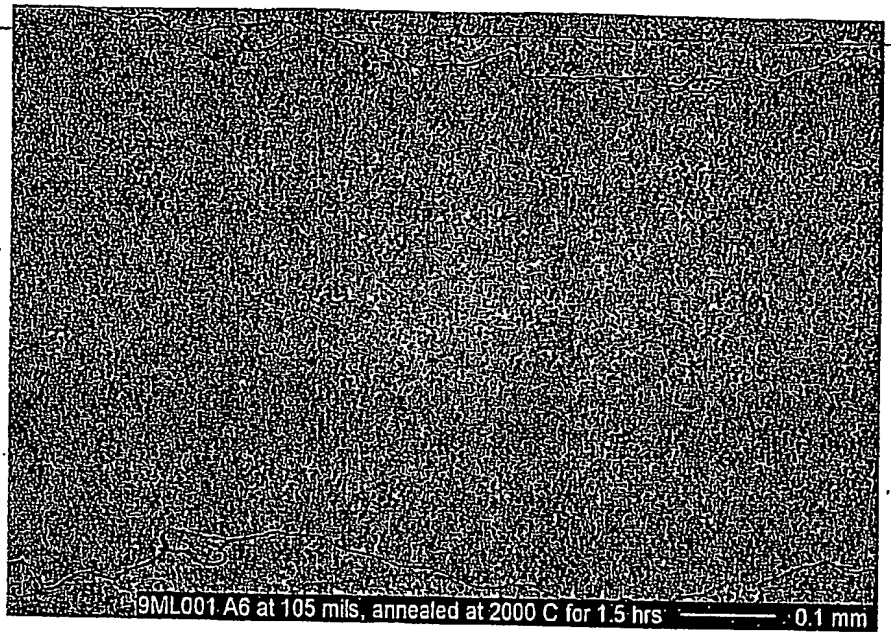

Figure 10: Microstructure of our ML material, deformed 8.7% and heat treated at 2000 C for 1.5 hours.

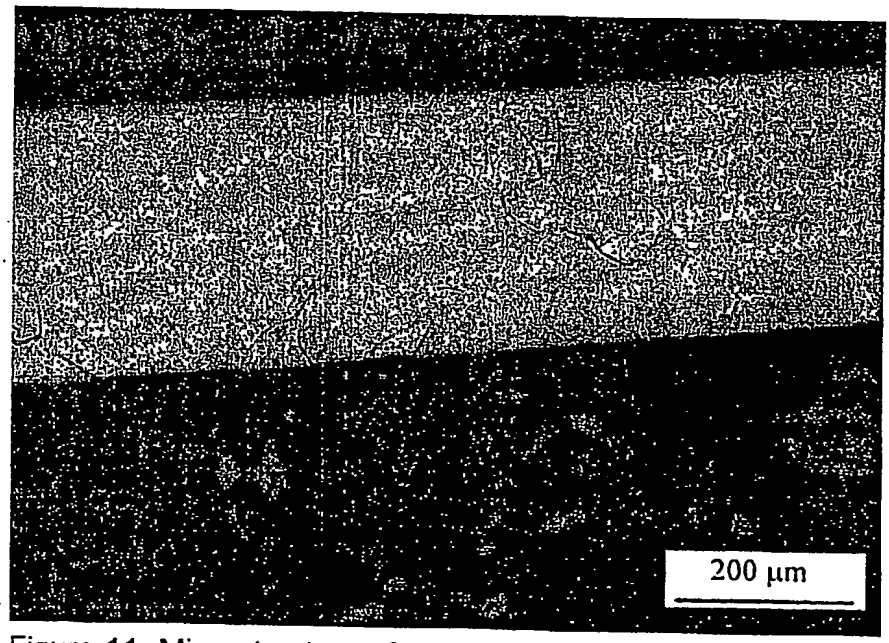

Figure 11. Microstructure of pure Mo material, deformed 96% and heat treated at 1900 C for 2 hours.

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DISCUSSION

Figure 3 shows a material that undergoes strain-induced grain boundary migration. The long grain boundary on the right hand side in the micrograph is the one "in action" eating up the smaller grain boundaries on its way. The 1800 C for 30 minutes heat treatment that the material received might not have been sufficient to remove the small grains of original material.

Figure 4 shows a material that undergoes strain-induced grain boundary migration. The higher % of cold work that this material received vs. the previous one makes this migrating grain boundary more potent in eating up the small grains of original material. The 1800 C for 30 minutes heat treatment was sufficiently high to remove the small grains.

Figure 5 shows a material that undergoes strain-induced grain boundary migration. Still higher % cold work this material received vs. previous one makes the number of potent migrating grain boundaries higher, hence the same heat treating conditions of 1800 C for 30 minutes provided higher number of grains. It can be speculated that 13.8% cold work this material received is either higher than the ξ_{crit} to achieve maximum grain size (red dot in Figure 1) or the heat treatment should be done at higher temperature.

Figures 6, 7 and 8 exhibit very similar microstructures. This indicates that the "tail" of the bell curve in Figure 1 (depicted as blue broken line) is very long and flat in the case of ML material, contrary to pure Al.

Figure 9 shows a recrystallized material, small equiaxed grains after heat treating a material that was 65% cold worked (region depicted as yellow dotted line in Figure 1).

Figure 10 shows the same material as in Figure 4, but heat treated at higher temperature and longer time. It seems that these new heat treating conditions provide for disappearance of some serrated, through thickness grain boundaries visible in Figure 4. In Figure 10 the grain boundaries are almost parallel to each other and tiny grains visible along those long grain boundaries will be finally "eaten up" given longer heating time and slightly higher treating temperature.

We did not have ML material available that was deformed more than 90% to verify the exaggerated grain growth phenomenon. However, we had a pure Mo foil available that was cold worked 96%. Hence we heat treated the foil at 1900 C for 2 hours. The microstructure of this material is shown in Figure 11. The exaggerated grain growth truly happened (a region depicted as green solid line in Figure 1).

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CONCLUSIONS

Using stress-induced grain boundary migration as the mechanism for grain growth, grain structures similar to structures observed in Plansee sheet were obtained. In addition, these grain structures were achieved without the cross-rolling of the sheet. Since the larger-interlocking grain structures resist creep, it is likely that boats for Exeter or other applications that require high creep resistance for high temperature service can be produced .

RECOMMENDATION

Since it is desirable to develop the most production friendly process, additional research work needs to be performed.

It is, therefore, recommended to:

- evaluate our ML material that was cold worked between 80 and 96% via appropriate heat treating
- make few trays for Exeter out of ML material that was cold worked in the strain-induced grain boundary migration region and few trays that were cold worked in the exaggerated grain growth region

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APPENDIX

Table I. Metalworking History of 9ML001 A6 Sample

Slab 2" thick (Mo-0.9 wt.% Lanthana)
Preheat at 2000F
Roll from 2" to 0.750" with reheats
Preheat at 1800 F
Roll from 0.750" to 0.250" with reheats
Preheat at 1450 F
Roll in perpendicular direction from 0.250" to 0.115" no reheats
Anneal at 975 C for 30 minutes
Anneal at 1150 C for 30 minutes
Material is stress and strain free – fully recrystallized, small recrystallized grains

Table II. Metalworking History of Pure Mo Sample Prior to 96% Cold Work.

Slab 2" thick (pur Mo 490 type powder)
Preheat at 2000 F
Roll from 2" to 1" with reheats
Anneal at 1050 C for 30 minutes
Preheat at 2000 F
Roll from 1" to 0.5" with reheats
Preheat at 1800 F
Roll from 0.5" to 0.250" no reheats
Anneal at 900 C for 30 minutes
Roll from 0.250" to 0.150" with one preheat at 400 C for 10 minutes
Anneal at 1075 C for 30 minutes
Material is stress and strain free – fully recrystallized, small recrystallized grains

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